

EXTRACTION OF DIBENZOTHIOPHENE FROM MODEL OIL USING IONIC LIQUIDS

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ABSTRACT

Diesel fuel in contrast has many benefits in our daily lives, which is use to power up vehicles and heavy machineries. Besides that, from the usage of diesel, it will produce sulfur when combustion is involved. Currently, Malaysia is making its effort to reach the sulfur target of 50 ppm as implemented by the Euro IV standards. Sulfur is very harmful towards humans, animals, machines and the environment. Sulfur contributes to air pollution by creating acid rains; in conjunction to machineries, it will corrode the equipment from the inside and thus reducing its effectiveness and requires a high cost to repair and maintenance. In this research, a sulfur compound called dibenzothiophene (DBT) is chosen as the study case. The objective of this research is to determine whether dibenzothiophene (DBT) can be extract or remove from model oil of n-hexane using an ionic liquid. The ionic liquid that is to be used is 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$. The ionic liquid is to be tested on a model oil of n-hexane to check its sulfur removal efficiency. A Fourier Transform Infrared Spectroscopy (FTIR) is conducted on the ionic liquid to check its content and an Infra-Red (IR) absorptions classification according to the wavelength is obtained to determine their functional groups. Next, the ionic liquid is tested on a Carbon Hydrogen Nitrogen and Sulfur (CHNS) analysis, to check its sulfur content. From the CHNS analysis, a manual calculation is to be done to check the molecular formula and compare it with the existing molecular formula, $C_6H_{13}N_2O_4S$. On top of that, a High Performance Liquid Chromatography (HPLC) analysis is conducted. A series of concentration for standard sample and sample is prepared. The samples consist of concentration in the range of 1500ppm to 250ppm. For the standard sample, the model oil of n-hexane is mixed with dibenzothiophene (DBT) is analyse and a calibration curve is plotted. For the sample, the ionic liquid is mixed with the model oil and dibenzothiophene (DBT) is analyse. From the data obtained it is then compared with the calibration curve and the sulfur removal efficiency is calculated. A bar chart for each of the concentration was plotted. From the result, it was found out that the sulfur removal is highly efficient at concentration of 1500ppm with 90.98%. In return of this work, perhaps a further research on diesel using ionic liquid will be conducted.

Key words: ionic liquid, extraction of sulfur, model oil, DBT

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1 INTRODUCTION

1.1 Motivation and statement of problem

The implementation of the revised law of clean air in USA has brought stricter limitation on sulfur content in petroleum products. The sulfur contents in new formula gasoline and clean diesel oil are required to be no higher than 100 and 500 mg/kg, respectively. Sulphur content will be reduced from the current 3000ppm standard to a new standard of a maximum of 50ppm. The sulphur content for Euro IV has been set at 50 ppm. Euro IV is an EU emission standard that was introduced in January 2005. The standard limits car emissions to 0.25g/km of NO_x (nitrogen oxides) and 0.02 g/km of PM (particulate matter). In order to meet Euro IV requirements, the country's refineries will have to upgrade their hydrotreatment units, to further remove sulphur from the fuel stream. All refineries are said to have now started the upgrading process. This shows that our country Malaysia putting an effort to reduce the emission of sulphur and help making earth a greener place to live in.

Diesel is a petroleum-based fuel that is used to empower many types of heavy vehicles and boats for transportation and many others in our daily lives. Diesel is made out of a blend of crude oil components which are hydrocarbons. Diesel are refined out of crude oil, usually by fractionate distillation. Diesel contains sulfur as part of their chemical makeup. However, sulfur is a compound that is poisonous to human. Sulfuric acid, as an example, is produced when sulfur combines with water vapor formed during the combustion process, where some of this corrosive compound is emitted into the atmosphere through the exhaust. Sulfuric acid is a major environmental pollutant, coming back to earth in contaminated rainwater. Besides that, in a study by McElroy et al. (2003), they studied that the sulfur speciation in diesel is an important task because sulphur-containing compounds create problems in poisoning of catalysts in refining; corrosion of pipelines, vessels, as well as engines.

Ionic liquid are materials that are composed solely of anions and cations. According to Yu-xin and Yong (2005), they conclude that the ionic liquids have been studied for possible applications related to green chemical processes, such as liquid/liquid extractions, gas separations, electro- chemistry and catalysis. In this research, they found out many advantages in applying an ionic liquid in their chemical process.

Besides that, they found out that ionic liquids are easy to handle because of nonvolatility, nonflammability, and high thermal stability. Hence, they pose little environmental harm which is very beneficial towards industrial processes.

In this research, the removal of sulphur compounds in model oil of n-hexane is studied using 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ as the ionic liquid.

1.2 Objectives

In this experiment, the objective is to determine the sulfur removal efficiency of dibenzothiophene in model oil of n-hexane using ionic liquid of 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$.

1.3 Scope of this research

In this experiment, there are a few elements to be tested.

- To extract dibenzothiophene using ionic liquid of 1-methylpyrazolium ethyl sulphate from model oil of n-hexane.
- To extract sulfur compounds from diesel using the ionic liquid.

1.4 Main contribution of this work

The following are the contributions of this work.

- It will help decrease air pollution on the environment.
- It will provide a valuable knowledge in making an effective ionic liquid to remove sulfur containing compounds.
- The ionic liquids is energy saving, time saving, and cost saving. It can be reuse and still have the effectiveness slightly as the first time used.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 is the literature review section which provides a brief description of the chemicals that will be using in this experiment. This section is the literature review which all the journal and all the citation will be. This section also describes the general view on diesel composition, dibenzothiophene, ionic liquid, and n-hexane. A brief

discussion on the journal is also provided. A summary on the journal will be discussed here.

Chapter 3 is the methodology part which all the procedure is stated step by step so that it is easy to be followed. A brief description on how the material and apparatus is obtained is discussed in that section.

Chapter 4 is the result part, where the result from the analysis is available here and will be further discussed in this section. The results will be compared with the results from all the journals to check whether it is valid.

Chapter 5 is the combine of the summary of the thesis and future work that will be done. This section also discussed on what to be improved from this research.

2 LITERATURE REVIEW

2.1 Overview

This paper shows the experimental studies of ionic liquids on the removal of sulfur containing compound from diesel or model oil. From their research, the ionic liquid is made out of a myriad of ions such as chlorine, sodium, iron and so on. After the synthesis of the ionic liquid, the ionic liquid is then tested on model oil which has been premixed with a selected sulfur containing compound to observe and study the removal effectiveness of sulfur. After that, the ionic liquid is then tested on diesel to see the result, and then compare it with the model oil.

2.2 Diesel composition

Diesel is a complex mixture of hydrocarbons with a boiling range from about 400 to 670°F. Besides that, it is also composed of hydrocarbons of three major classes: paraffinic, naphthenic, and aromatic hydrocarbons. In an analysis of diesel done by some researcher, the biggest setback is the separation and identification of pure compounds or classes of compounds from the complex hydrocarbon mixtures in diesel. The analysis uses the fluorescent indicator analysis method (FIA; ASTM D-1319) to separate and quantify saturates, olefins and aromatic hydrocarbons in diesel fuels. Another approach is to determine aromatic content by nuclear magnetic resonance spectroscopy, (NMR). These methods do not give the same result because they do not measure the same properties (Thomas, et al. 1991). Further study on diesel is done and a wide variety of sulfur compounds was detected.

On the other hand, in a work presented by a number of researchers which was to determine sulfur compounds in diesel using Gas Chromatography (GC). In this work, it was known that a mixture of standard substances containing thiols, sulfides, thiophenes, benzothiophenes, dibenzothiophenes and benzonaphthothiophenes was present in diesel. Besides that, by using a one-dimensional chromatography it requires a very high column efficiency and stability in retention time of substances to avoid errors of the identification. On the flipside, by using a two-dimensional chromatography it easier and more reliable be identified due to the substance can be determined by both X- and Y-axis (Wei et al. 2003).

Furthermore, a study based on the removal of thiophenesulfide from diesel is done. In this research, the researchers agreed that the sulfur in the fuels are hazardous, which not only pollute environment but also corrode equipments. Therefore, sulfur removal from fuels becomes an increasing technical challenge in refinery industry. On top of that, the difficulty of sulfides removal is closed related to the sorts of sulfides. The active sulfides such as hydrogen sulfide and thiols are easy to remove, but nor to the inactive sulfides with aromatic rings such as thiophene and its derivatives (Xin and Yong, 2005)

Table 2.1: Status of Fuel Quality on Asia-Pacific Region

Country	Sulfur (Max, ppm), Diesel	50ppm Target Date
China	2,000	2016
India	500	No Date
Indonesia	3,500	No date
Malaysia	500	2016
Philippines	500	2010
Republic of Korea	50	2012
Singapore	50	2012
Thailand	500	2012
Vietnam	500	2016

Source : Asia-Pacific Petrol & Diesel Sulphur Matrix, 2012

Table 2.1 shows the sulfur content emission for selected Asia-Pacific country. It is known that some of the country has reached its target of 50ppm of sulfur content for diesel emission. The European Standard has named this target as Euro IV.

In another statement, whereby a study case done in the USA, a group of researcher found out that, a common problem that faces the refineries around the world is that the crude oils are getting worse and heavier with sulfur content getting higher. However,

sulphur emission is imposing an urgent requirement on refineries to reduce the sulfur content in the fuels they produce (Hua, et al. 2003).

Table 2-2:Status of Fuel Quality on Asia-Pacific Region

Name	7000 ppm	1200 ppm	120 ppm
MST	1099	19	0
BT	0	0	0
C1BT	9	0	0
C2BT	88	3	0
C3BT	391	17	0
C4BT	477	24	0
C5BT	468	29	0
C6BT	457	35	0
C7BT	470	41	0
C8BT	457	44	0
C9BT	364	43	0
C10BT	328	41	0
C11BT	247	33	0
C11+BT	152	25	0
C0DBT	83	7	1
C1DBT	306	91	3
C2DBT	503	234	23
C3DBT	484	250	34
C4DBT	315	156	23
C5DBT	222	103	16
C6+DBT	164	81	12
Total	7085	1277	111

* Abbreviations : MST, mercaptan, sulphide, and thiophene; BT, benzothiophene; and DBT, dibenzothiophene.

Source: Wang et al. 2003.

From Table 2-2, it is clearly stated that the sulfur compound in diesel is indeed exist. For this research, it is important to test an ionic liquid whether it is capable to remove or extract sulphur by evaluate it first on a model oil n-hexane which containing dibenzothiophene (DBT) as sulfur containing compound. By testing it on the model oil, it is to determine the effectiveness of the removal of sulfur. From the testing, it is then evaluated whether it can proceed on the real fuel such as diesel. This is to reduce the wastage of diesel because it is a non-renewable source.

2.3 *1-Methylpyrazolium Ethyl Sulphate*

This is the ionic liquid that will be using in this experiment. This ionic liquid is obtained from University Teknologi PETRONAS (UTP), due to the insufficient of chemical to synthesis the ionic liquid.

Table 2.3: Physical properties of 1-methylpyrazolium ethyl sulphate

Molecular formula	C ₆ H ₁₃ N ₂ O ₄ S
Molecular weight	209 g/mol
Physical state	Colourless Liquid
Melting point	167-169°C
Solubility in water	Insoluble

Source: www.chemicalbook.com

From table 2.3, it shows a brief description on the physical properties of the ionic liquid. This ionic liquid is colourless liquid. It must be handle with care because the limited supply of ionic liquid.

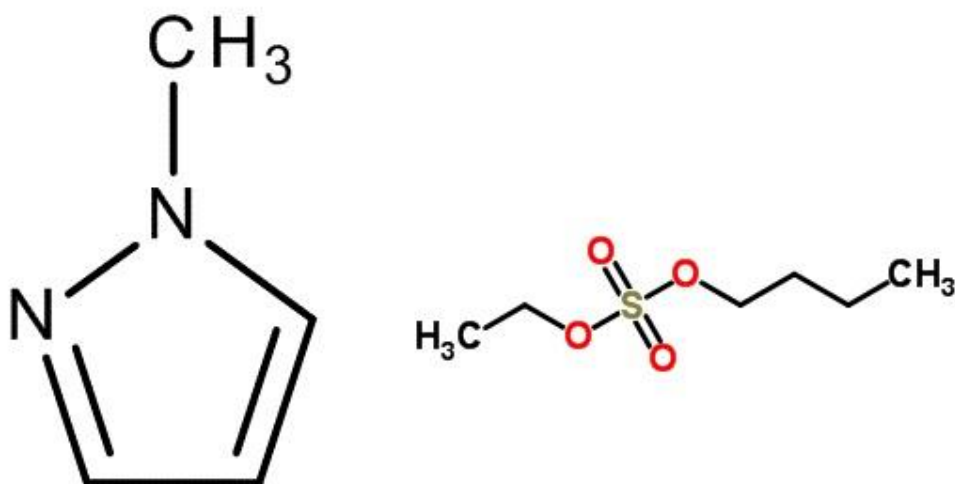


Figure 2.1: Molecular structure of 1-methylpyrazolium ethyl sulphate

2.4 Dibenzothiophene

Dibenzothiophene (DBT) is an organic sulfur compound that consists of two benzene ring and a sulfur ring in the middle. It is mostly available in a white powder form. DBT may cause eye irritation and skin irritation when handling, hence it is advisable to wear protective gear. It is also insoluble in water.

Table 2.4: Physical properties of dibenzothiophene

Molecular formula	$C_{12}H_8S$
Molecular weight	184.26 g/mol
Physical state	Crystalline powder
Density	1.252 g/cm ³
Melting point	97-100°C
Boiling point	332-333°C
Solubility in water	Soluble

Source: apps.wku.edu

Table 2.4 shows the physical properties of dibenzothiophene. From the source, it stated that DBT is prepared by the reaction of biphenyl with sulfur dichloride in the presence of aluminium trichloride. This sulfur compound is premixed with the ionic liquid to determine the sulfur removal efficiency of the ionic liquid.

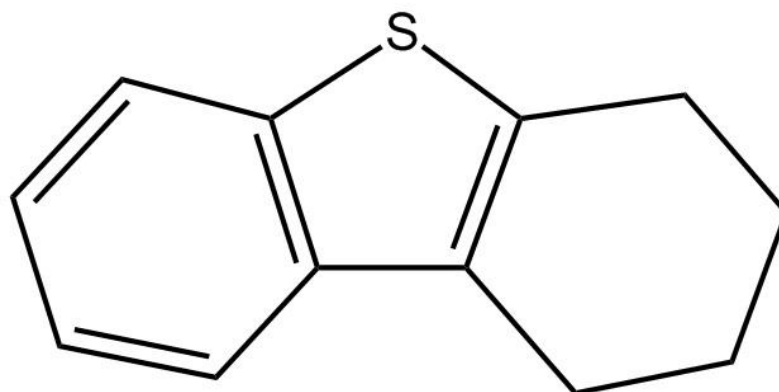


Figure 2.2: Molecular structure of dibenzothiophene

2.5 Thiophene

Thiophene, also known as thiofuran, is a cyclic compound containing four carbon atoms and one sulfur atom in the ring. Thiophene is an analog to furan and pyrrole where the sulfur atom is replaced by O and NH respectively. Thiophene is a toxic, flammable, and colorless liquid. It is also insoluble in water.

Table 2.5: Physical properties of thiophene

Molecular formula	C ₄ H ₄ S
Molecular weight	84.14
Physical state	Clear liquid
Melting point	-38°C
Boiling point	83-84°C
Specific gravity	1.06
Solubility in water	Insoluble

Source: www.chemical21.com

From table 2.5, it shows some of the physical properties of thiophene. From the source, it stated that thiophene is the simplest aromatic compound containing sulfur atom and it shares some similar chemical properties with benzene. The lone electron pairs on sulfur in the delocalized pi electron system does not exhibit the properties of thioethers but

aromaticity. The sulfur atom is unreactive but the adjacent carbons are susceptible to attack by electrophiles. It is reactive toward sulfonation. Most of the reseachers are using thiophene as their experimental sulfur compound.

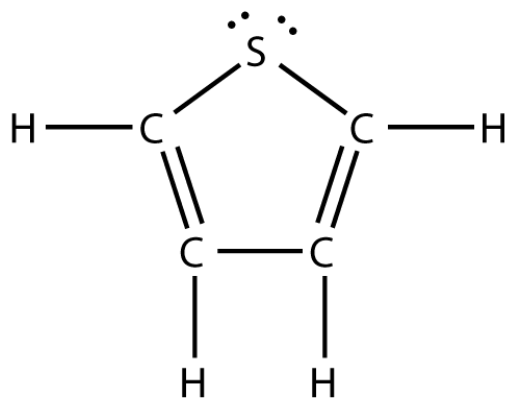


Figure 2.3: Molecular structure of thiophene

2.6 *n*-hexane

n-hexane is selected as the model oil in this research. This chemical, *n*-hexane has been chosen due to the availability and the low risk level when handling this chemical.

Table 2.6: Physical properties of *n*-hexane

Molecular formula	C ₆ H ₁₄
Molecular weight	86.17536
Density	0.660 g/cm ³ at 20°C
Boiling point	68.95°C
Water solubility	Insoluble in water

Source: <http://www.atsdr.cdc.gov>

From Table 2.6, it shows some of the physical properties of *n*-hexane. *N*-hexane is a very volatile aliphatic hydrocarbon. *N*-hexane is colourless liquids at room temperature, odourless when pure. It is cheap, relatively safe, largely unreactive and easily evaporated.



Figure 2.4: Molecular structure of *n*-hexane

2.7 *Ionic liquids for synthesising*

Chemistry is dominated by the study of species in solution, for example, a liquid. Although any liquid may be used as a solvent, only a few of that liquid can be used. So far as we know, water is a general solvent. In a study done by a researcher, he found out that, some simple physical properties of the ionic liquids that make them interesting as potential solvents for synthesis are the following: Firstly, they are good solvents for a wide range of both inorganic and organic materials. Secondly, they are composed of poorly coordinating ions, so they have the potential to be highly polar. Thirdly, they are immiscible with some organic solvents and provide a nonaqueous, polar alternative for two-phase systems. For immiscible polar phases containing hydrophobic ionic liquids, it can also be used with water. Fourthly, they are nonvolatile, hence they may be used in

high-vacuum systems and eliminate many containment problems (Welton, 1999). Hence, it's safe to say that the synthesis ionic liquids can be used in this research.

Table 2.7: Modern ionic liquids

A salt	Cation and or anion quite large
Freezing point	Preferably below 100°C
Liquid range	Often > 200°C
Thermal stability	Usually high
Viscosity	Normally < 100 cP
Dielectric constant	Implied ≤ 30
Polarity	Moderate
Specific conductivity	Usually < 10 mS cm ⁻¹ , "Good"
Vapor pressure	Usually negligible

Source : Welton, 1999.

From table 2.7, shows the properties of some selected modern ionic liquids. It is known that ionic liquid exhibits a good quality and safe chemical when synthesising.

The application of ionic liquids in synthesis and catalysis are widely used nowadays. In a research done by a researcher, he found several factors that ionic liquids is better than conventional liquids which are, firstly, synthetic chemists are limited by the available molecular solvents in which they can conduct chemistry. Secondly, most of the solvents chemists like to use are banned by international protocols determined to reduce pollution, of which volatile organic compounds represent a significant part. Thirdly, the discovery of new chemistry or the ability to design a solvent that allows a specific reaction to occur (Wasserscheid and Welton, 2008). Hence, the reason he stated above

maybe because fact that ionic liquids are perceived as “green” material which do not pollute the environment.

2.8 Experimental works on ionic liquid

In this section, this paper presents a myriad of experimental works of ionic liquids on the removal of sulfur content in some compound. In a work done on sulfur removal from fuels using ionic liquids, the researchers uses 3 ionic liquids which were 1-Ethyl-3-Methylimidazolium Tetrafluoroborate ($\text{EMIM}^+\text{-BF}_4^-$), 1-Butyl-3-Methylhexfluorophosphate ($\text{BMIM}^+\text{-PF}_6^-$) and 1-Butyl-3-Methylimidazolium Tetrafluoroborate ($\text{BMIM}^+\text{-BF}_4^-$). In the used ionic liquids, the molar ratio of thiophene to ionic liquid was found to be 0.86/1, 3.5/1 and 2.2/1 for $\text{EMIM}^+\text{-BF}_4^-$, $\text{BMIM}^+\text{-PF}_6^-$, $\text{BMIM}^+\text{-BF}_4^-$. It was found out that for a specific aromatic compound, for example thiophene, $\text{BMIM}^+\text{-PF}_6^-$ and $\text{BMIM}^+\text{-BF}_4^-$ have higher absorption capacities than $\text{EMIM}^+\text{-BF}_4^-$. The results suggest that the structure and the size of both cation and anion of an ionic liquid affect absorption. The local structure of the ionic liquids appears to have a significant effect on their interaction with the aromatic compounds (Zhang and Zhang, 2002).

In another interesting study, several researchers have conducted an experiment on the enhanced oxidative desulfurization of model fuels using a film-shear reactor. The researchers uses benzothiophene in decane, it was found out that 53% of the benzothiophene was removed from the model fuel in only 80s at 10°C using the film-shear reactor. It was then conclude that the application of a film-shear reactor provides a remarkable enhancement in the efficiency of the ODS process compared to normal stirring. Experiments reported here demonstrate that the amount of benzothiophene in a model fuel can be rapidly reduced (Fox et al. 2011).

In another findings by some researcher on the extraction of nitrogen and sulfur containing air pollutants from model oil. They studied on do-decane and pyridine, it was found out that the effect of the ionic liquid-to-oil ratio, and the extraction capacity improved as the ratio of IL-to-oil was increased for pyridine. Besides that, the extraction of sulfur compounds from the model oil demonstrated that the concentration of the S-compound in the model oil was reduced by 99% after a completed extraction. This result demonstrated that the extraction of dibenzothiophene from the model oil, with 1-

ethyl-3-methylimidazolium chloride ([C2 mim] [Cl]) was successful (Anugwom et al. 2011).

There was also another study on desulfurization using ionic liquids by several researchers, where FeCl_3 [Iron (III) Chloride], was chosen to check its sulfur removal efficiency on n-dodecane. From their research, they conclude that FeCl_3 showed the better sulfur removal efficiency than other ionic liquids. This experiment clearly demonstrates that the extraction ability of [Bmim]Cl/ FeCl_3 is suitable in comparison with the other ionic liquids. It was also found that the extraction process went on quickly. It has the effectiveness of 75.6%. In general FeCl_3 alone exhibited lower extraction ability than the Fe-containing ILs, signifying the important role of [Bmim]Cl (Dharaskar et al. 2013).

Besides that, in a recent study on desulfurization of fuels using ionic liquid based on FeCl_3 [Iron (III) Chloride], the researchers uses 10 types of Lewis acid ionic liquids. 3 of the 10 types of the ionic liquids use were [BMIM]Cl/ FeCl_3 (BMIM: 1-Butyl-3-Methylimidazolium), [OMIM]Cl/ FeCl_3 (OMIM: 1-Octyl-3-Methylimidazolium), $\text{T}_8\text{Cl}/\text{FeCl}_3$ (T_8Cl : Tri-Octyl Methyl Ammonium Chloride). In the study on extraction of dibenzothiophenes (DBT) in n-Octane, it was found out that [BMIM]Cl/ FeCl_3 yield the highest extractive performance for DBT which was 67.6%. By comparing it to the other 10 types of ionic liquid, the use of FeCl_3 shows promising extraction rather than using ZnCl_2 [Zinc Chloride], MnCl_2 [Manganese (II) Chloride] and etc. On top of that, Fe-IL system shows considerable promise for providing a future needs for low sulfur diesel (Wang et al. 2008).

In an another research on the removal of 4,6- dimethyldibenzothiophene (DMDBT), the researchers tested the work on n-dodecane and formaldehyde vapour as reactive adsorbent. It was found that the desulfurization efficiency increased when the temperature ranged from 50°C to 80°C . The presence of formaldehyde caused 100% removal of 4,6-DMDBT in 90 min at 80°C but only 8.14% in three hours in its absence. It was concluded that the sulfur capacities of the reactive adsorbent were closely related to formaldehyde as well as the type of fuel. The presence of formaldehyde in the adsorbent makes a difference to the desulfurization capacity, which results from the polymerization degree of the sulfurs (Yu et al. 2012). Therefore, the temperature difference plays a role on how the ionic liquids behave when reacting with the solvent.

On the other hand, a recent study done by researchers, it was on the extraction of dibenzothiophene from dodecane using ionic liquids. It was found out that, among all the 18 ionic liquids that were tested, the imidazolium based ionic liquids with thiocyanate, dicyanamide and octylsulfate anions exhibited the highest extraction capabilities with 66.1%, 66.1%, and 63.6% of extraction efficiency respectively. From their observation, the π - π interaction between aromatic rings of sulfur compound and ionic liquid (IL) was not be the main extraction mechanism. A trend between specific volume and desulfurization efficiency of ILs was discovered, enabling them to predict IL's desulfurization efficiency from its specific volume. Besides that, it was found that IL can be reused in extraction without regeneration with considerable desulfurization efficiency. High energy saving can be achieved if this IL is used, instead of regenerating IL after every time of extraction (Wilfred et al. 2011). It can be said that, by recycling the IL can be time saving and energy saving because it can reduce the production of waste in conducting this experiment.

Furthermore, also there was a study done by researchers on the effect of n-containing molecules on the hydrodesulfurisation (HDS) of dibenzothiophene (DBT). It was a studied on the influence of 2-methylpyridine and 2-methylpiperidine on the HDS of dibenzothiophene (DBT) over a sulfided NiMo/Al₂O₃ catalyst. It was found out that, basic N-containing compounds have been characterized among the strongest inhibitors for HDS. Their experiment showed that the presence of any amount of N-containing molecule in the feed completely blocks the hydrogenation pathway of the DBT HDS, so that the only product observed is biphenyl. 2-Methylpiperidine is a much stronger base than 2-methylpyridine. At 1:1 and 1:2 ratios of DBT to 2-methylpiperidine the conversion of DBT hardly changed. 2-Methylpiperidine did not convert to any products (Egorova and Prins, 2002). Their experimental works was not successful and maybe a further research is needed to make it work in the future.

In addition, a study on the complex extraction of thiophenes using room temperature ionic liquids was conducted by some researchers. Two kinds of room temperature ionic liquids (RTILs) 1-butyl-3-methylimidazolium chloroaluminate (III) ([bmim]ClAlCl₃) and 1-butyl-3-methyl imidazoliumhexfluorophosphate ([bmim]PF₆) were synthesized. The ionic liquids is then tested on the removal of thiophenes from refined diesel by the method of complex extraction. From the result obtained, it showed that under the best operational conditions, the content of thiophenes decline 46 wt% in chloroaluminate

RTIL and 69 wt% in hexfluorophosphate RTIL. The diesel was improved at the same time. The two kinds of RTILs can be used for several times through regenerating (Yuxin et al. 2007). It can be concluded that, even at room temperature the ionic liquids can performed effectively and the is no set back in this experiment.

On top of that, a study on the extractive desulfurization and denitrogenation of fuels using ionic liquids was conducted by a researcher. In the experiment, there were two types of ionic liquids, 1-alkyl-3-methylimidazolium [AMIM] tetrafluoroborate and hexafluorophosphate and trimethylamine hydrochloride (AlCl_3 -TMAC). It was tested to see its potential for sulfur removal from transportation fuels. EMIMBF₄ (E = ethyl), BMIMPF₆ (B = butyl), BMIMBF₄, and AMIMPF₆. These four ions showed high selectivity, particularly toward aromatic sulfur and nitrogen compounds, for extractive desulfurization and denitrogenation. For BMIMBF₄ the highest sulfur removal percentage was 14% which was “DBT and pyridine in n-C12”. AlCl_3 -TMAC ionic liquids were found to have remarkably high absorption capacities for aromatics which were 20% sulfur removal (Zhang et al. 2004). Hence, it can be strongly agree that these ionic liquid indeed have a high percentage of sulfur removal efficiency when mixed with sulfur compounds.

On the contrary, a study on the desulfurization of gasoline by extraction with new ionic liquids was done by some researchers. In this experiment, 1-butyl-3-methylimidazolium chloride was synthesis and studied with CuCl-based ionic liquid. The structure is checked under fast atom bombardment mass spectrometry (FAB-MS). It was found out that, CuCl₂, Cu₂Cl₃ and Cu₃Cl₄ existed in the ionic liquid. From the result obtained in this experiment, CuCl-based ionic liquid shows remarkable desulfurization ability in the desulfurization of gasoline when used as an extraction absorbent. For BMIMCu₂Cl₃ the highest sulfur removal was at 37.4% with the sulfur content in oil to be treated was 196 ppmw (Huang et al. 2004) . It can be confirmed that the chlorine based ionic liquids has a higher percentage of sulfur removal efficiency.

Next, a study on the deep oxidative desulfurization of diesel fuels by acidic ionic liquids was done by some researchers. In this experiment, intensive research on the removal of thiophenicsulfur species from diesel fuels and six functional acidic ILs are studied, in which ILs are used as both extractant and catalyst. Lewis acidic species such as 1-butyl-3-methylimidazolium chloride/2ZnCl₂ ([C₄mim]Cl/2ZnCl₂ and [C₄mim]Cl/ZnCl₂) and

Brønsted acidic species such as 1-methyl-3-ethylcarboxylic acid imidazolium hydrogen sulfate ($[\text{CH}_2\text{COOHmim}]\text{HSO}_4$), 1-methyl-3-(butyl-4-sulfinate) imidazolium hydrogen sulfate ($[\text{SO}_3\text{H-C}_4\text{mim}]\text{HSO}_4$), $[\text{Hmim}]\text{HSO}_4$, and $[\text{C}_4\text{mim}]\text{HSO}_4$. From all these IL, it was found out that $[\text{C}_4\text{mim}]\text{Cl}/2\text{ZnCl}_2$ can reduce the sulfur content in real commercial diesel fuel from 64 to 7.9 ppm with a sulfur removal of 87.7%; however, it is not too effective for coke diesel fuel with high initial sulfur content of 5380 ppm (Yu et al. 2011). It can be concluded that, once again the chlorine type ion has a higher efficiency in helping to remove sulfur compounds.

There was also a study on the optimization of oxidative desulfurization of dibenzothiophene using acidic ionic liquid as catalytic solvent done by some researchers. In the experiment, the oxidative desulfurization of dibenzothiophene (DBT) in *n*-octane as model oil with Brønsted acidic ionic liquids (ILs) N-methylpyrrolidonium phosphate ($[\text{Hnmp}]\text{H}_2\text{PO}_4$) as catalytic solvent. By which 99.8% of DBT in the model oil was removed under the optimal conditions. The desulfurization efficiency of actual diesel was 64.3% under the optimized conditions. From their evaluation, the desulfurization efficiency of DBT decreased when oxidation temperature > oxidation time > molar ratio of H_2O_2 /sulfur (O/S) > volume ratio of ($[\text{Hnmp}]\text{H}_2\text{PO}_4$) to model oil (Zhao et al. 2009). It can be said that, the temperature plays a role in the reaction with diesel by mixing with ionic liquids.

2.9 Summary of literature review

From the journal reviewed, it can be concluded that ionic liquid plays a major role in removing sulfur. It is highly effective be it in model oil, model fuel or in diesel and any other organic liquids. In one of the journal, it was also found out that the ionic liquid have a very unique characteristic, where the ionic liquid can be recycled and still performs better and consistent when reuse to remove sulfur from a model oil. This is very good because the supply of the ionic liquid in this research is very limited. On top of that, most of the ionic liquid use in their research shows the sulfur removal efficiency of more than 50%. This shows that the ionic liquid is very effective. Hence, this research on model oil of *n*-hexane by using ionic liquid of 1-methylpyrazolium ethyl sulphate $\text{C}_6\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ should show the same result.

3 MATERIALS AND METHODS

3.1 Overview

This paper presents a process or procedure on how the extraction of dibenzothiophene from model oil will be conducted. Besides that, a total of 3 analysis will be conducted which are Fourier Transform Infrared Spectroscopy (FTIR) Analysis, Carbon Hydrogen Nitrogen Sulfur (CHNS) Analysis, High Performance Liquid Chromatography (HPLC) will be used in this experiment to assist the expected result and the result obtained later on. The ionic liquid of 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ is to be used and studied for its sulfur removal efficiency. On the other hand, the model oil that was chosen is n-hexane. The ionic liquid will be premixed with dibenzothiophene (DBT). Furthermore, it will be tested based on main manipulator which is the concentration.

3.2 Introduction

This section consists of a step by step procedure on how to conduct this experiment. The chemical is advised to be handling with care due to insufficient chemical to restock the chemicals. All protective gears must be worn to avoid misshaped in conducting this experiment due to all the chemical used is hazardous towards human when come in contact or exposed for a period of time.

3.3 Chemicals and Apparatus

The ionic liquid, 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ is obtained from University Teknologi PETRONAS (UTP), due to the insufficient supply chemicals and the unavailability of equipment in University Malaysia Pahang (UMP) laboratory that is needed to synthesis the ionic liquid. The model oil, n-hexadecane and Dibenzothiophene (DBT) are obtained from UMP laboratory.

The apparatus that will be using in this experiment are obtained from the laboratory. Some of the apparatus that will be using is conical flasks, measuring cylinder, electronic weight machine, incubating shaker; and all the other standard equipment are available in the laboratory.

3.4 Methodology

i. Preparation of n-hexane as model oil

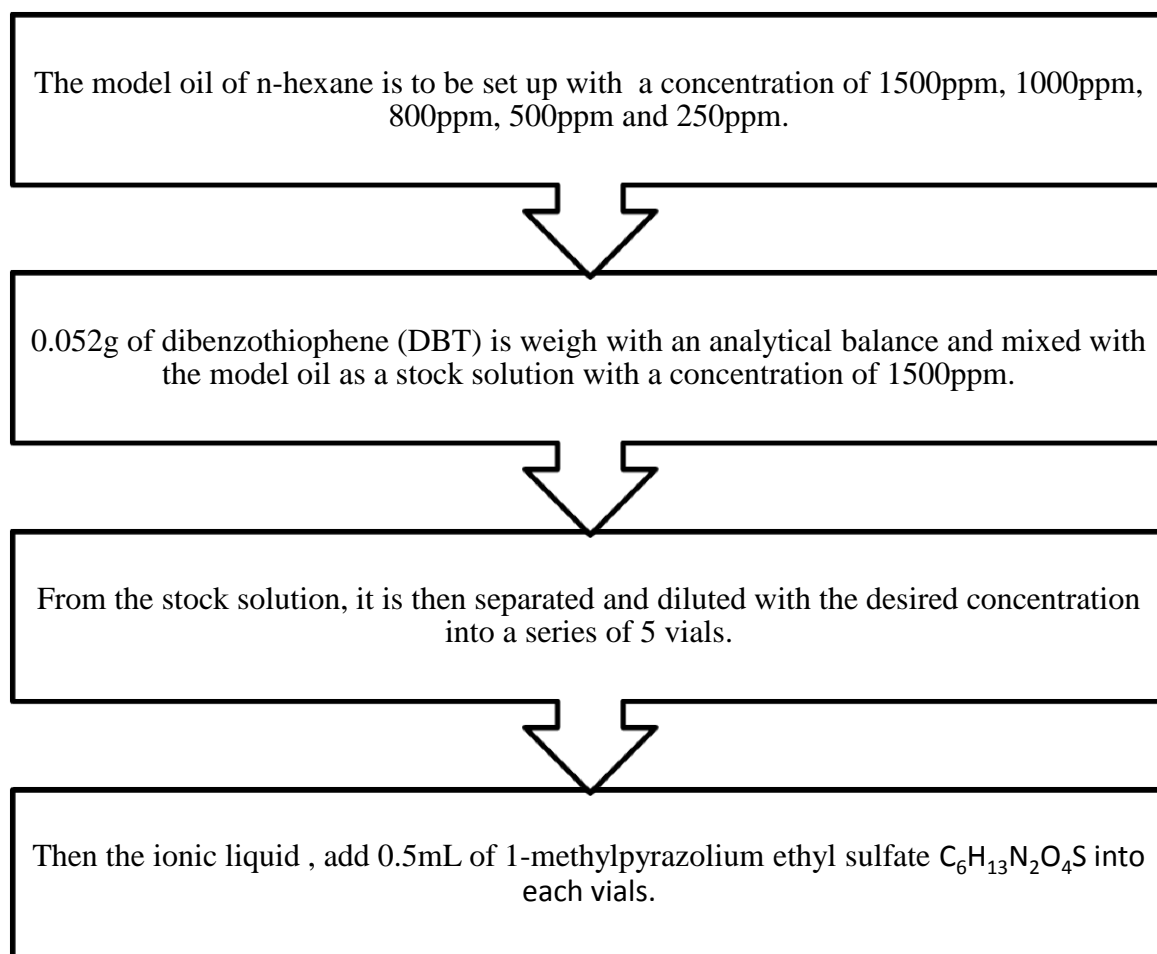


Figure 3.1: Process flow for preparation of model oil of n-hexane

Firstly, n-hexane was prepared by dissolving dibenzothiophene (DBT) in n-hexane to give solutions with sulfur contents of 1500ppm. A 0.052g of dibenzothiophene (DBT) is weigh with an analytical balance. A series of concentration of 1000ppm, 800ppm, 500ppm and 250ppm is needed to make from the stock solution of 1500ppm. Next, the concentration is put into a series of 5 vials. After that, the ionic liquid 1-methylpyrazolium ethyl sulfate $C_6H_{13}N_2O_4S$ of 0.5mL is added into each vials. Then, the vials are check with HPLC to see the sulfur removal efficiency.